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Simultaneous Catalytic Removal of NO and N_2O using Fe–MFI

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Fe–MFI preparations active for the reduction of nitric oxide and nitrous oxide with hydrocarbons have been prepared by solid-state ion-exchange in the presence of air. While nitrous oxide can be removed by a variety of reducing agents, C_3 hydrocarbons, especially propane, are suitable for the catalytic reduction of nitric oxide. The reduction of nitrous oxide was always enhanced by increasing temperature, whereas maximum NO conversions were observed at temperatures around 300°C. The addition of up to 7% of water was found to decrease the achievable conversions of the nitrogen oxides moderately. The activity for the removal of nitrous oxide was strongly inhibited in the presence of NO, probably via an intermediate formed from NO_2 and the hydrocarbon. On the other hand, the observed NO conversions were not affected by the presence of nitrous oxide. In all cases, considerable amounts of carbon monoxide were formed from the hydrocarbons. It could be shown that the degree of ion-exchange achievable during the solid-state procedure is limited. At iron contents exceeding Fe/Al = 0.5, Fe ions are no longer being introcuded into the zeolite. The excess iron is being precipitated as hematite, which is inactive in the reduction of both nitric oxide and nitrous oxide.

INTRODUCTION

Despite promising catalytic activities for the reduction of nitrogen oxides with hydrocarbons, zeolite-based catalysts have not yet been commercialized for this purpose due to a lack of long-term stability, especially in the presence of sulphur dioxide and water vapor (1). Recent results indicate that iron exchanged MFI zeolites exhibit remarkable stability under realistic off-gas conditions. Feng and Hall (2, 3) reported high catalytic activities during the reduction of NO with *iso*-butane that even exceeded the performance of Cu–MFI. The achievable conversions at 500°C were not decreased in the presence of 20% H_2O and 150 ppm SO_2. Although the extremely high catalytic activities claimed by Feng and Hall could not be reproduced by other groups (4–6), Fe–MFI appears to be less inhibited by water vapor and hydrothermally more stable than other exchanged zeolite catalysts. Chen and Sachtler clearly demonstrated that high activities for the reduction of nitric oxide with *iso*-butane under wet conditions remain for at least 100 h on stream at 350°C. A slight deactiviation was shown to be caused by a reversible deposition of carbonaceous material rather than by destruction of the zeolite matrix or the active iron species (5).

An interesting feature of Fe–MFI is furthermore that not only NO but also N_2O can be reduced to nitrogen by using hydrocarbons. Concern about nitrous oxide emissions has recently increased due to the reported potential of this component in global warming and stratospheric ozone depletion (7). Segawa and co-workers (8, 9) used propene as reductant and achieved high nitrous oxide conversions, also in the presence of oxygen and up to 15% water. Since several industrial exhaust gases such as nitric acid off-gases and flue gases from fluidized-bed combustions contain significant amounts of NO_x and N_2O (7), it appears straightforward to test Fe–MFI for the simultaneous removal of both pollutants. We have shown briefly in an earlier contribution that substantial conversions of NO and N_2O can be achieved simultaneously, using propane as reducing agent (6).

One reason for the late discovery of the high catalytic activity of Fe–MFI catalysts in nitrogen oxides removal is the difficulty in introducing iron into zeolites. Delgass *et al.* (10, 11) have shown that Fe^{2+} ions are easily oxidized in aqueous medium giving rise to the formation of iron hydroxide species. Consequently, most active Fe–MFI preparations described so far have been obtained under anaerobic conditions. Feng and Hall (3) used iron oxalate in a glass apparatus with separate supply of zeolite and iron salt under nitrogen atmosphere. These authors claimed to have obtained iron loadings as high as Fe/Al = 1.0 mol/mol. In an attempt to reproduce these results by using a similar apparatus, Chen and Sachtler (4) achieved much lower degrees of ion-exchange. A more reproducible method of introducing iron was found to be the sublimation of a volatile iron salt, $FeCl_3$, into the cavities of the hydrogen form of the parent zeolite under inert atmosphere (4, 5). Pophal *et al.* employed iron sulphate during aqueous ion-exchange at 50°C under nitrogen (8, 9). The achievable degree of ion-exchange was limited to about Fe/Al = 0.4. Farnos *et al.* (12) used the same aqueous method, but pointed out that temperatures above

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80°C were advantageous with respect to the iron loading of the zeolite, because increasing temperatures were believed to reduce the size of the hydration sphere of the Fe^{2+} cation. However, Chen and Sachtler (4) have clearly shown that the activity of iron exchanged MFI zeolites in the reduction of nitric oxide with hydrocarbons is strongly dependent on the nature and history of the parent zeolite used, if aqueous procedures are employed. Very recently, Hall *et al.* have confirmed these problems in preparing Fe–MFI catalysts (13).

Since all described techniques require the absence of oxygen, it is obviously difficult to develop a commercial catalyst preparation based on these methods. We have thus used the solid-state ion-exchange procedure proposed by Karge and Beyer (14, 15) to prepare iron exchanged MFI zeolites. Varga *et al.* (16) employed this method to obtain Fe–MFI, but no catalytic tests were carried out. Dandl (17) used iron exchanged MFI catalysts prepared by solid-state ion-exchange under vacuum during the decomposition of nitrous oxide. In our earlier communication (6) we already showed that active Fe–MFI preparations can be obtained by solid-state ion-exchange even in the presence of air, a method that can be transferred without difficulties to the large-scale manufacture of catalysts. In the present paper we report on detailed catalytic tests of Fe–MFI during the reduction of NO_x and N_2O with hydrocarbons. Special attention was paid to the possibility of simultaneously removing both nitrogen oxides under realistic off-gas conditions.

EXPERIMENTAL

Catalyst Preparation and Characterization

The Fe–MFI catalysts were prepared by solid-state ion-exchange of commercial MFI zeolite (AlSi-PENTA, SM 27, Si/Al = 11.4, Fe/Al = 0.007) in the ammonium form. Thus 3 g of zeolite were mechanically mixed with $FeCl_2 \cdot 4\,H_2O$ in a ball mill for at least 1 h. The resulting mixture was heated to 550°C within 3 h and maintained at this temperature for 6 h in the presence of air. The iron exchanged catalysts were washed with water and dried at 110°C for 16 h. The standard preparation was adjusted to a molar Fe/Al ratio of 0.75. Furthermore, a series of catalysts with Fe/Al ratios of 0.007 (iron content of H–MFI obtained by calcination of NH_4–MFI) to 1.5 was prepared. It was shown earlier (6) that no iron is lost during solid-state ion-exchange and calcination. For comparison, a Fe_2O_3/Na–MFI sample with Fe/Al = 0.75 was prepared by mechanically mixing $FeCl_2 \cdot 4\,H_2O$ and Na–MFI (AlSi-PENTA, SN 27, Si/Al = 11.4), followed by calcination and washing as described above. X-ray diffraction (XRD) measurements were carried out by using a Siemens diffractometer with Cu$K\alpha$ radiation. The micropore volume of the samples was determined by adsorption of nitrogen at 77 K using a standard BET system.

Reaction Studies

The selective catalytic reduction of NO and N_2O with hydrocarbons was carried out in a continuous flow apparatus. In all cases, a 315- to 500-μm catalyst sieve fraction was used after pretreatment in flowing helium at 500°C. The catalysts (400 to 1600 mg) were placed in an electrically heated quartz reactor. The temperature was regulated by using a thermocouple in the center of the catalyst bed. Additionally, the temperature of the reactor wall at the same axial position was monitored by means of a second thermocouple. Typical gas mixtures supplied by thermal mass flow controllers (Brooks, 5850) consisted of 1000 ppm NO, 1000 ppm N_2O, 4% O_2, and 1000 ppm hydrocarbon (e.g. C_3H_8). Then, 10% of the nitric oxide added were converted to nitrogen dioxide after admixture of oxygen in the lines upstream the reactor. It was possible to prevent the NO oxidation by heating the lines or by means of oxygen addition directly at the reactor entrance. However, the use of a NO/NO_2 reactant mixture allowed for the observation of interesting differences between the reactions of nitric oxide and nitrogen dioxide. Up to 7% water could be added to the reactant stream by means of a saturator. A total volume flow rate of 400 cm^3/min was employed in all measurements. The exit concentrations were measured by using a magnetomechanic oxygen analyzer (Hartmann und Braun, Magnos 4), infrared analyzers for NO, N_2O, CO, and CO_2 (Rosemount, Binos 4), and a UV photometer for NO_2 (Rosemount, Binos 5). During the measurements, steady-state exit concentrations were obtained after 15 to 30 min. The hydrocarbon conversion was calculated from the exit CO and CO_2 concentrations, while the CO selectivity is defined as the amount of carbon monoxide formed related to the amount of hydrocarbon converted.

RESULTS AND DISCUSSION

Use of Different Reducing Agents

In a preliminary series of measurements, three different hydrocarbons, methane, propane, and propene, were used as reductants during the simultaneous removal of N_2O and NO at GHSV = 30,000 h^{-1} by using the standard catalyst with Fe/Al = 0.75. Figure 1 shows the conversions of nitrous oxide, of NO_x (nitric oxide and nitrogen dioxide) to nitrogen, and of the hydrocarbon as a function of the temperature in the catalyst bed. The reaction mixture consisted of each 1000 ppm NO, N_2O, and hydrocarbon together with 4% O_2 (balance He). Due to the exothermic reactions taking place, the temperature in the center of the catalyst bed was up to 10 K higher than that at the reactor wall at complete conversion of the C_3 hydrocarbons. It can be seen that nitrous oxide can be removed with all reductants used above 450°C. With descending temperatures, the N_2O conversion decreases. Methane is the least effective

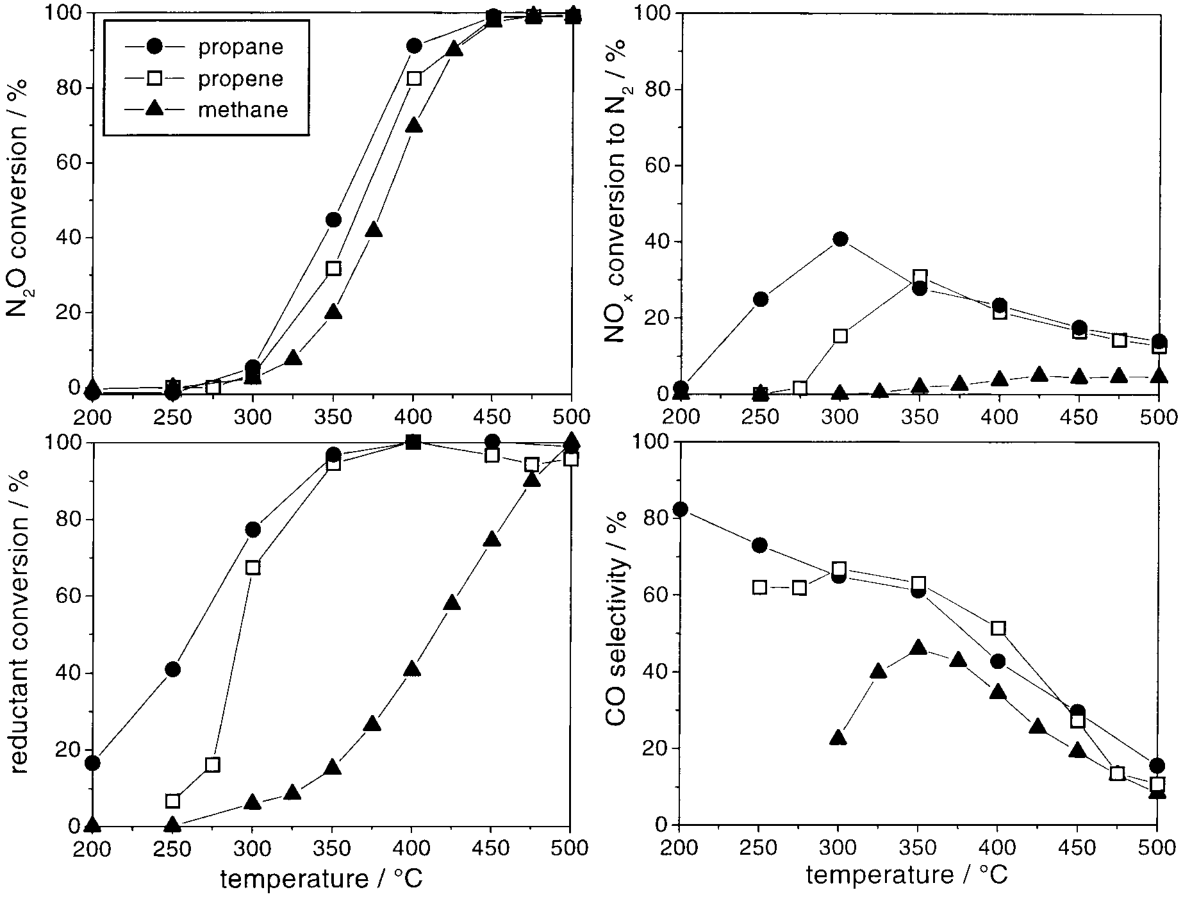

FIG. 1. Effect of temperature on conversions of N_2O, NO_x to N_2, and hydrocarbons, as well as on CO selectivity. Feed: 1000 ppm NO, 1000 ppm N_2O, 1000 ppm hydrocarbon, 4% O_2 in He with 400 mg of catalyst (Fe/Al = 0.75), i.e., GHSV = 30,000 h^{-1}.

hydrocarbon, especially when the very low achievable NO_x conversions of less than 5% and the poor conversions of CH_4 itself are taken into account. The use of propene and propane gives rise to relatively similar results. However, slightly higher nitrous oxide conversions and a higher maximum NO_x conversion (40% at 300°C) are observed with the alkane. In all cases, undesirable carbon monoxide is being formed in side reactions, the CO selectivity being especially high in the low temperature region. For all further measurements, propane was selected as the most effective reducing agent.

Influence of Space Velocity

The following measurements were carried out with 1000 ppm C_3H_8 as reductant at different space velocities. At the lowest space velocity of 7500 h^{-1}, the temperature difference between the center of the catalyst bed and the reactor wall reached up to 20 K. It can be seen that the nitrous oxide conversion is not dependent on the space velocity while the conversions of NO_x to nitrogen and of propane increase as expected with increasing catalyst mass (Fig. 2). Interestingly, the highest NO_x conversions are observed in the range of temperature 250 to 300°C, which is lower than the optimum temperatures reported by Chen and Sachtler (4, 5) and even up to 150 K lower than the respective temperatures determined by Feng and Hall (2, 3, 13). Both groups, however, used *iso*-butane as reductant. Apparently negative N_2O conversions in the low temperature region are due to the formation of small amounts of nitrous oxide during the reduction of NO_x, where the nitrous oxide in the feed is no longer being converted. This interpretation was confirmed by measuring the product composition during NO reduction in the absence of N_2O in the feed. Figure 2 also shows that the maximum of the CO selectivity is shifted to lower temperatures at decreasing space velocities. This result can be easily explained by the subsequent oxidation of carbon monoxide, which is enhanced by higher temperature and catalyst mass.

The NO_2 exit concentrations (not shown) at elevated temperatures are higher than the inlet concentration of ca. 100 ppm. This additional formation of nitrogen dioxide is strongly enhanced by the decrease of space velocity. On the other hand, NO_2 reacts to nitrogen at lower temperatures.

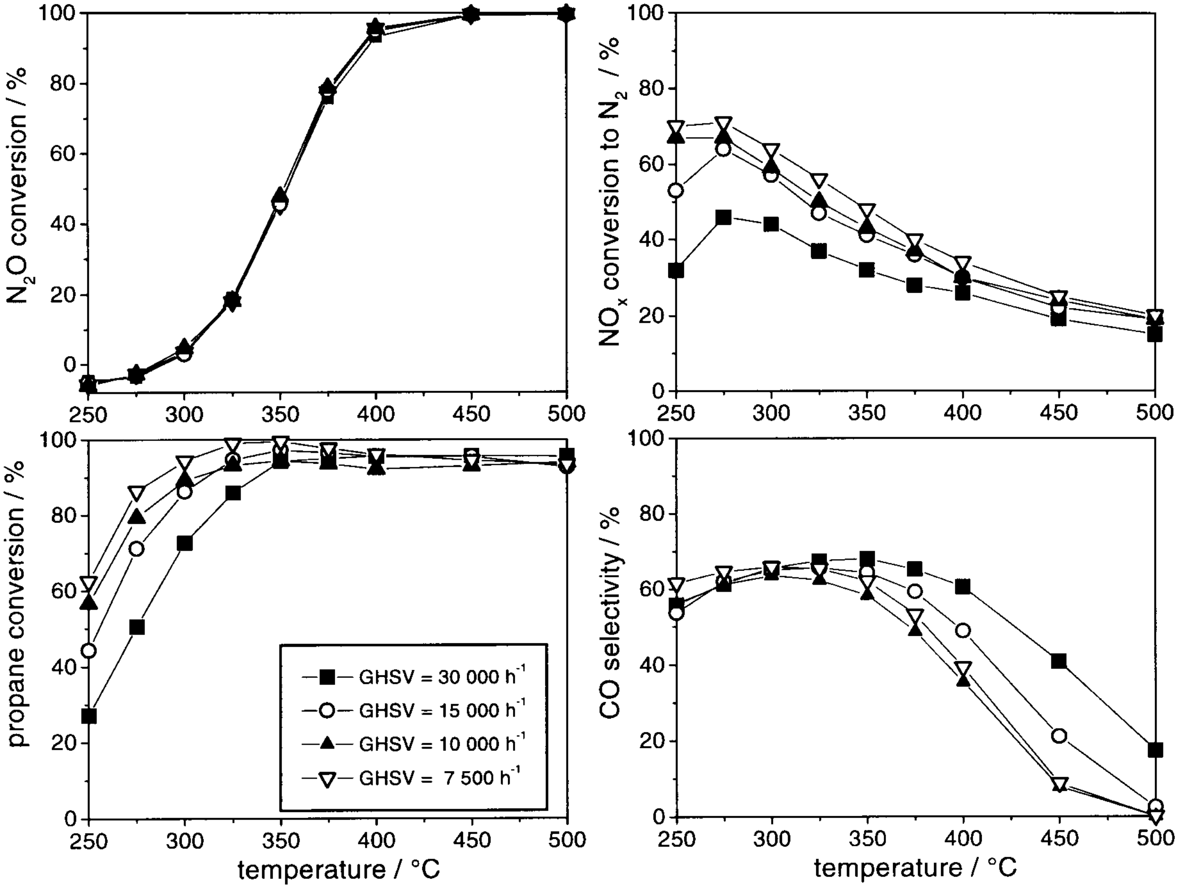

FIG. 2. Conversions of N_2O, NO_x, propane, and CO selectivity versus temperature at different space velocities. Feed: 1000 ppm N_2O, 1000 ppm NO, 1000 ppm C_3H_8, and 4% O_2 in He using 400, 800, 1200, and 1600 mg of catalyst (Fe/Al = 0.75), respectively.

Between 250 and 300°C, where maximum NO_x conversions can be observed (Fig. 2), it is almost completely converted to nitrogen. Thus, it is highly probable that nitrogen dioxide is an intermediate during the reaction of NO to N_2 as it has been proposed by many researchers for other zeolite catalysts active in the hydrocarbon reduction of nitric oxide (18–20).

On the other hand, the missing effect of space velocity on the conversion of nitrous oxide is not easy to understand. The minor amounts of N_2O formed from NO at low temperatures cannot compensate the enhanced conversion of N_2O at decreasing space velocities. Results obtained during the N_2O reduction in the absence of NO_x in the feed clearly show the expected response to an increase in catalyst mass. In that case, N_2O conversions of 80% can be achieved at 300°C and a space velocity of 7500 h^{-1}, while less than 10% of the nitrous oxide is converted in the presence of 1000 ppm NO_x in the feed (Fig. 2). It is possible that the presence of NO or NO_2 limits the conversion of nitrous oxide, but this can be ruled out experimentally. When a mixture of each 1000 ppm NO and N_2O together with 4% oxygen is passed over the catalyst, nitrous oxide is as effectively converted to nitrogen as in the presence of hydrocarbons (cf. Fig. 1). At the same time, nitric oxide reacts to NO_2. Thus, neither nitrogen oxides nor the hydrocarbon alone appear to be responsible for the strong detrimental effect on the N_2O conversion as well as the missing effect of space velocity. Recent results by Sachtler and co-workers (21) offer a plausible explanation for our experimental observations. It could be shown that the formation of nitrogen during the reduction of NO with hydrocarbons over Fe–MFI catalysts requires the presence of a carbonaceous deposit formed from nitrogen dioxide and the hydrocarbon. During this step, a reduced form of nitrogen is obtained that reacts with another molecule of nitrogen dioxide to yield dinitrogen. If this scheme holds, a strongly adsorbed, reactive intermediate formed from NO_2 and propane may be responsible for the decrease in catalytic activity with respect to the reduction of nitrous oxide.

Influence of Water Content

Figure 3 shows the results of the simultaneous reduction of N_2O and NO at a space velocity of 7500 h^{-1} using water concentrations of up to 7%. It can be seen that the addition

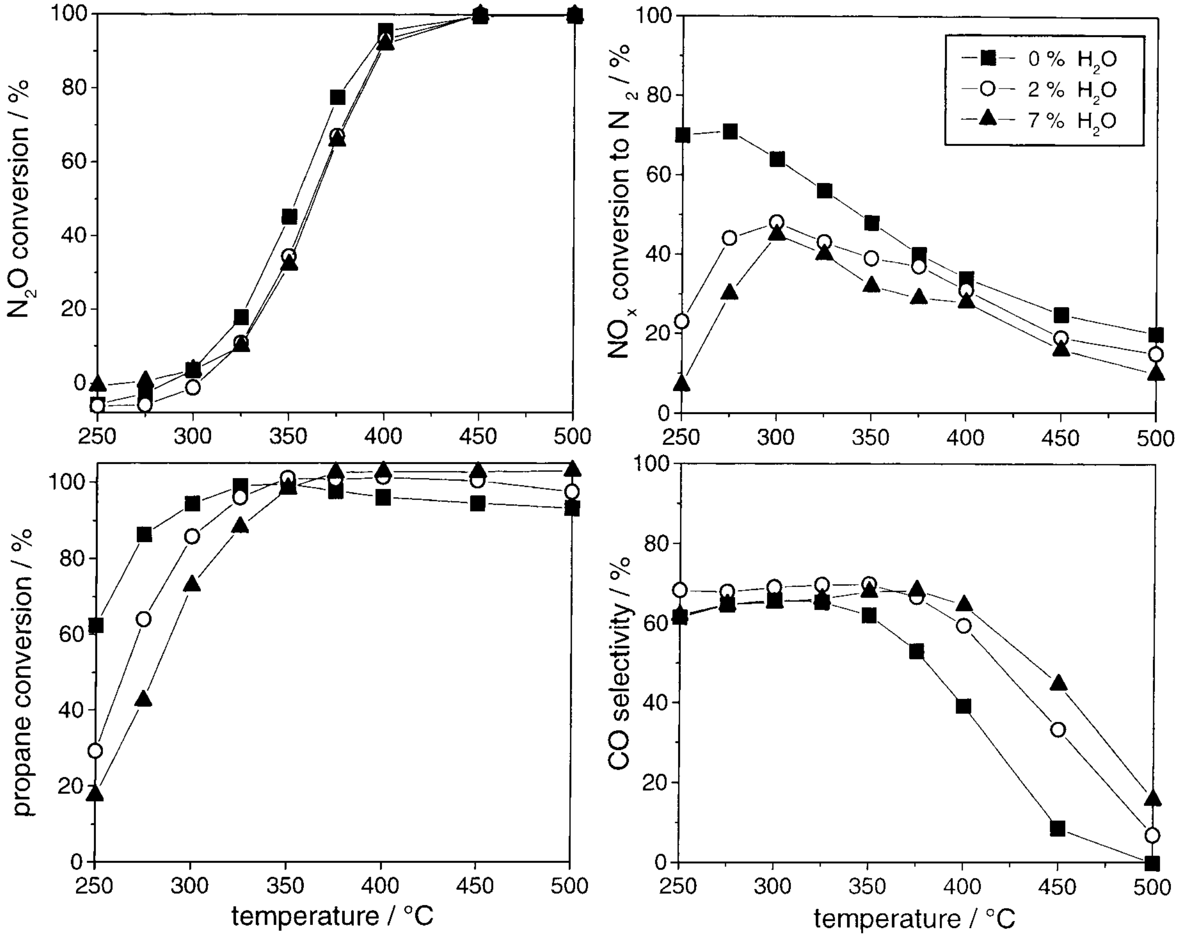

FIG. 3. Conversions of N_2O, NO_x, propane, and CO selectivity versus temperature obtained at GHSV = 7500 h^{-1} in the presence of different water concentrations. Feed: 1000 ppm N_2O, 1000 ppm NO, 1000 ppm C_3H_8, and 4% O_2. Catalyst mass 1600 mg (Fe/Al = 0.75).

of water has hardly any influence on the N_2O conversion. The conversion of nitric oxide and nitrogen dioxide to nitrogen is moderately decreased at temperatures above 300°C, but a stronger decrease in NO_x reduction activity can be observed at temperatures below this value. This is contrasting to results reported by Chen and Sachtler (4, 5) during the catalytic reduction of NO with *iso*-C_4H_{10}, where even an enhancement of activity at low temperatures upon addition of H_2O occurred. The responses of propane conversion and CO selectivity to addition of water (Fig. 3) also show that the catalytic activity of the Fe–MFI used is decreased in the presence of water vapor. On the other hand, measurements in the absence of NO_x (Fig. 4) show a much more pronounced detrimental effect of water addition on the nitrous oxide conversion than in the presence of NO_x (Fig. 3). Thus, the proposed intermediate formed from NO_2 and propane seems to inhibit the conversion of N_2O stronger than the presence of water.

In Fig. 5, the conversions of nitrous oxide and NO_x in the presence and absence of the second nitrogen oxide under otherwise constant conditions are compared. The decrease of the N_2O conversion in the presence of NO can be clearly seen, while the NO_x conversion to nitrogen remains almost unaffected whether nitrous oxide is being added or not. From these results it is obvious that the hydrocarbon reduction of NO and N_2O must follow completely different reaction schemes. NO is reduced in a complicated mechanism involving adsorbed nitrogen dioxide and hydrocarbon species as proposed by Sachtler and co-workers (21). On the other hand, it can be assumed that the formation of N_2 from nitrous oxide requires the split of the N-O bond on the active iron species followed by removal of adsorbed oxygen via reaction with reducing agents.

Influence of Propane Concentration

The results obtained so far show that the optimum temperature for the reduction of NO is around 300°C, whereas the N_2O conversion is steadily increasing with increasing temperature, reaching complete conversion at around 400°C. Thus, the most suitable temperature for a simultaneous removal of both pollutants appears to be in the region

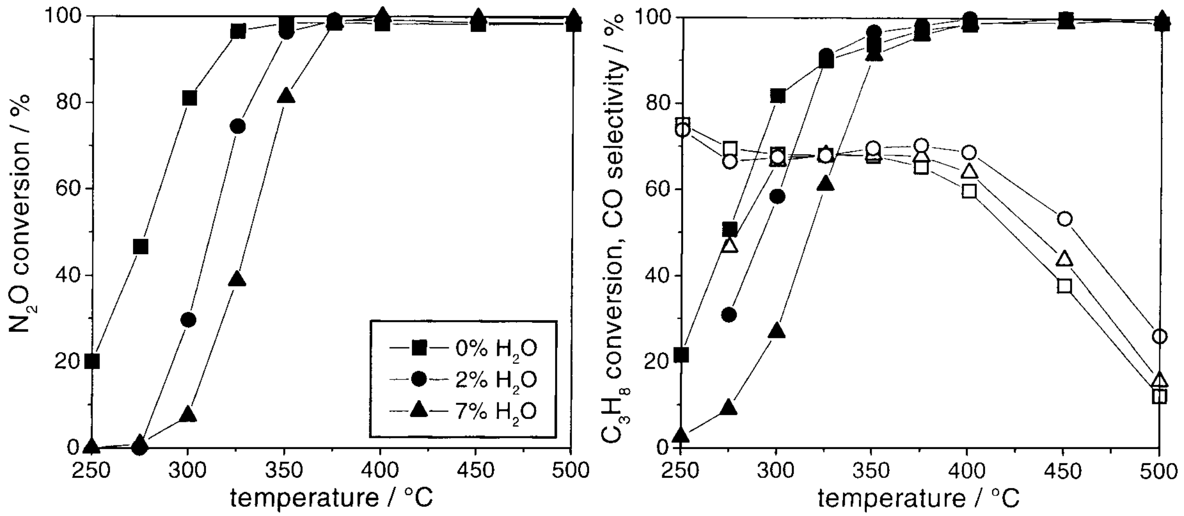

FIG. 4. Conversions of N_2O, propane (closed symbols), and CO selectivity (open symbols) versus temperature at GHSV = 7500 h^{-1} and different water concentrations. Feed: 1000 ppm N_2O, 1000 ppm C_3H_8, and 4% O_2. Catalyst mass 1600 mg (Fe/Al = 0.75).

of 350°C. At this intermediate temperature, the effect of reductant concentration on the nitrogen oxides conversions was investigated at GHSV = 7500 h^{-1} in the presence of 7% H_2O. Figure 6 shows that the achievable N_2O and NO_x conversions are strongly increasing when higher propane concentrations are employed. At 5000 ppm C_3H_8 in the feed, about 80% of the nitrous oxide and 90% of nitric oxide and nitrogen dioxide can be converted to N_2 even in the presence of water vapor. On the other hand, the propane conversion is no longer complete at concentrations exceeding 1000 ppm, reaching a value of only 70% at 5000 ppm C_3H_8. The carbon monoxide selectivity is not influenced by variation of the propane concentration and remains constant at 65%. It is interesting to note that the CO selectivities during all measurements are in the range between 60 and 70%, while only at temperatures higher than 400°C significantly lower values can be observed.

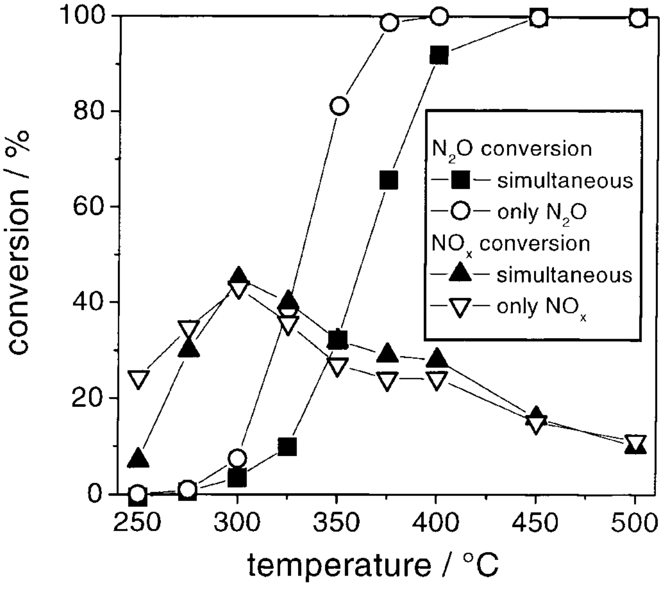

FIG. 5. N_2O and NO_x conversion as a function of temperature at GHSV = 7500 h^{-1} in the presence and absence of the second nitrogen oxide. Feed: 1000 ppm N_2O and/or NO, 1000 ppm C_3H_8, 4% O_2, and 7% H_2O. Catalyst mass 1600 mg (Fe/Al = 0.75).

The fact that the NO_x conversion increases stronger than the N_2O conversion is probably due to temperature effects. The measured differences between the temperature in the center of the catalyst bed (350°C) and the reactor wall were between 5 K (500 ppm propane) and 30 K (5000 ppm propane). Thus, it is possible that the average catalyst temperature is slightly decreasing with increasing propane inlet concentration giving rise to an enhancement of the NO_x conversion (cf. Fig. 3) whereas the N_2O conversion is less positively affected.

Variation of Iron Content

It has been reported earlier (6) that the standard catalyst with a molar ratio of Fe/Al = 0.75 not only contains ion-exchanged iron but also a fraction of iron oxide (hematite). For investigation of the catalytic activity of the different iron species present in Fe–MFI catalysts, samples with different iron content were compared. Furthermore, H–MFI obtained by calcination of the parent NH_4–MFI zeolite and a Fe_2O_3/Na–MFI sample with Fe/Al = 0.75 were also subjected to the simultaneous reduction of N_2O and NO_x with propane. Figure 7 shows that the Fe_2O_3/Na–MFI catalyst is completely inactive both for the removal of nitrogen oxides and the oxidation of propane. H–MFI exhibits lower activities with respect to the conversion of N_2O and C_3H_8. The maximum NO_x conversions over H–MFI and the different Fe–MFI catalysts are similar (ca. 50%), but this maximum

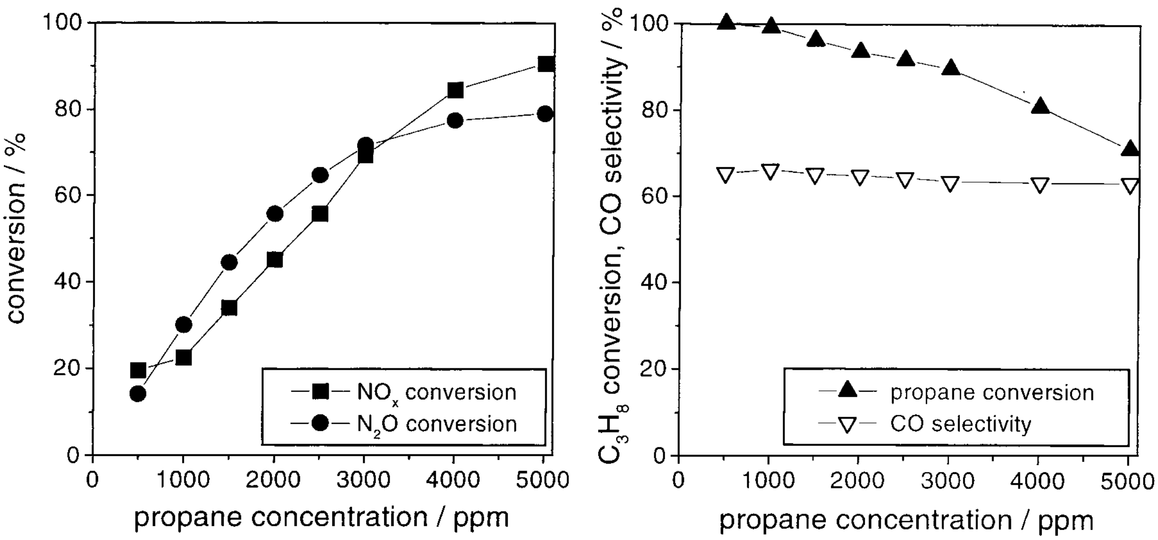

FIG. 6. Influence of propane concentration on N_2O, NO_x and propane conversions as well as on CO selectivity during the simultaneous removal of nitrous oxide and nitric oxide at 350°C and GHSV = 7500 h^{-1}. Feed: 1000 ppm N_2O, 1000 ppm NO, 500 to 5000 ppm C_3H_8, 4% O_2, and 7% H_2O. Catalyst mass 1600 mg (Fe/Al = 0.75).

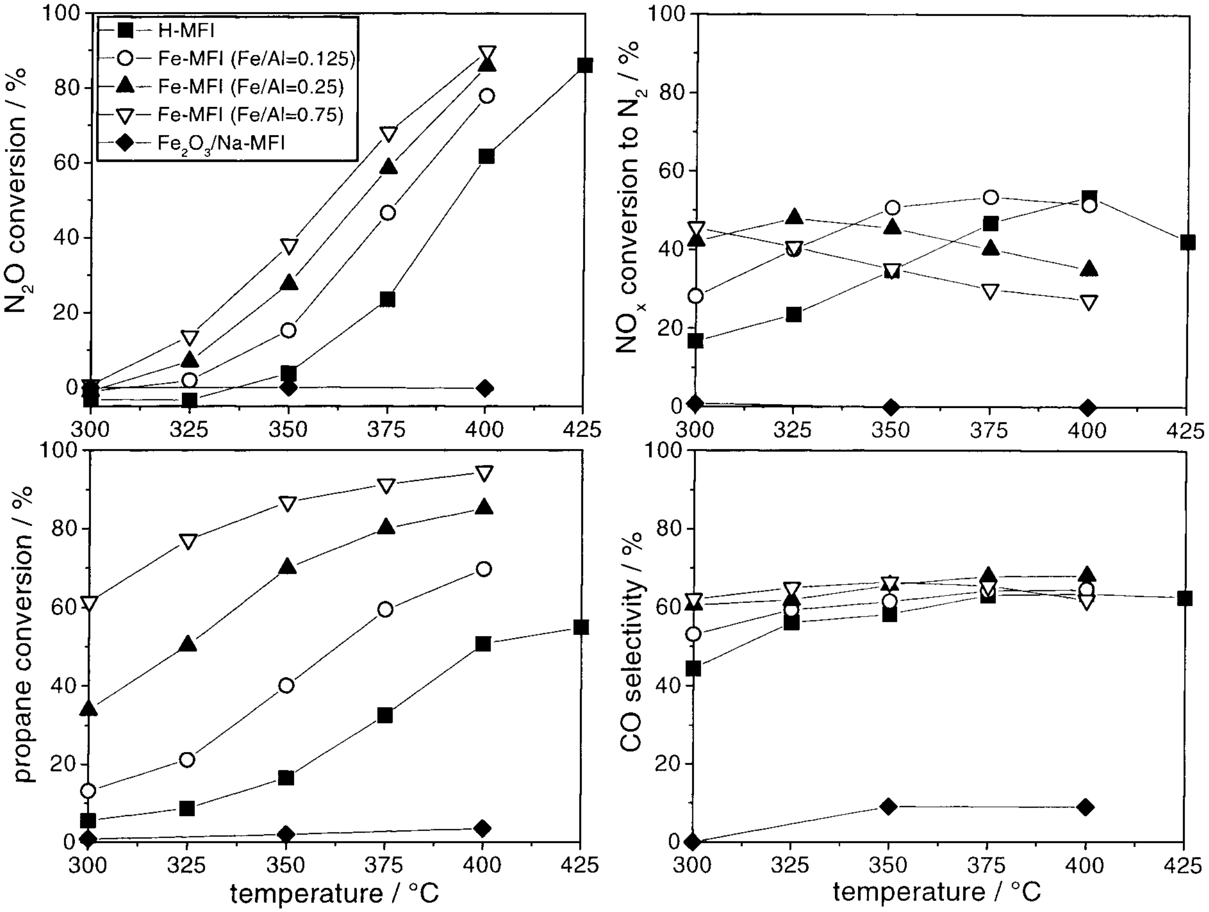

FIG. 7. Conversions of N_2O, NO_x, propane, and CO selectivity obtained at GHSV = 30,000 h^{-1} using different catalysts. Feed: 1000 ppm N_2O, 1000 ppm NO, 1000 ppm C_3H_8, and 4% O_2. Catalyst mass 400 mg.

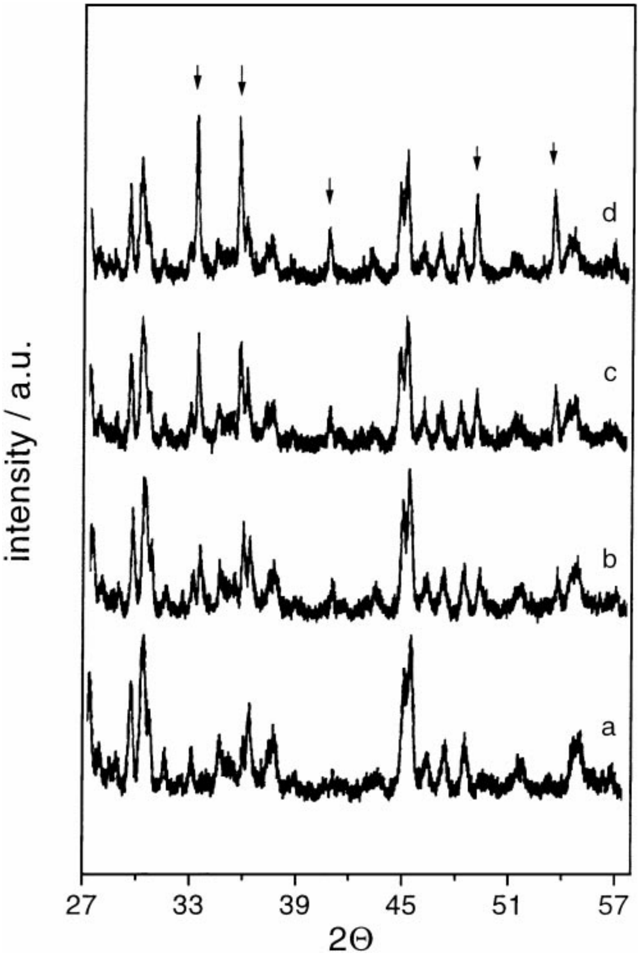

FIG. 8. XRD patterns of calcined catalysts with different iron content. The arrows denote Fe_2O_3 (hematite). (a) H-ZSM-5, (b) Fe/Al = 0.25, (c) Fe/Al = 0.5, (d) Fe/Al = 0.75.

is shifted to lower temperatures with increasing iron content of the catalyst. It has to be noted that up to 40 ppm of N_2O are being formed over H–MFI at temperatures (300 to 350°C) where no such formation occurs when Fe–MFI catalysts are used. Both nitrous oxide and propane conversion are also clearly enhanced by an increase in iron content. Thus it appears that the active species in Fe–MFI catalysts are Fe ions and that the degree of ion-exchange can be increased by increasing the amount of iron chloride used during the solid-state ion-exchange. However, the amount of iron ions introduced by the solid-state procedure is limited. An increase of catalytic activity can only be observed up to about Fe/Al = 0.5. At higher ratios (up to Fe/Al = 1.5), only iron species being inactive in the reactions studied appear to be formed.

Characterization of the catalysts confirms these findings. Figure 8 shows the XRD patterns of samples with different Fe/Al ratio. It can be seen that hematite is already formed in the sample with Fe/Al = 0.25 and that the amounts of iron oxide present in the catalysts appear to increase with ascending Fe/Al ratio. Nevertheless, the pore volumes of the samples determined by nitrogen adsorption reveal that the pores in the catalysts remain accessible even at Fe/Al = 0.75 (0.147 cm^3/g compared to 0.155 cm^3/g for H–MFI). The precipitation of hematite probably occurs on the outer surface of the zeolite crystals. Further studies are needed to determine the degree of ion-exchange in catalysts prepared by solid-state ion-exchange and to elucidate the role of acid and metal sites in the reduction of nitrogen oxides with hydrocarbons over Fe–MFI.

In comparison, solid-state ion-exchange in the presence of air and anaerobic aqueous procedures as described by Pophal *et al.* (8) probably give rise to about the same degrees of ion-exchange. The solid-state procedure requires the preparation of ammonium zeolites in an additional exchange step. However, this is current industrial practice in zeolite manufacture. On the other hand, oxygen must be carefully excluded when aqueous ion-exchange methods are employed. Overall it is thus believed that a large-scale process for the preparation of Fe–MFI catalysts can be more easily developed based on solid-state ion-exchange.

CONCLUSIONS

The catalytic reduction of nitrous oxide and nitric oxide with hydrocarbons in the presence of excess oxygen and water vapor was carried out over Fe–MFI catalysts. It could be shown that active preparations can be obtained by solid-state ion-exchange without the necessity of excluding air during the procedure. With an increasing amount of iron present in the catalysts, the activity increases up to a ratio of Fe/Al = 0.5. Even with this iron content, however, a fraction of iron is present as hematite in the catalysts, as could be confirmed by XRD measurements.

The optimum temperature for NO removal was found to be surprisingly low at around 300°C, whereas the conversion of N_2O steadily increased with ascending temperature. While the NO conversions were not affected by the presence of N_2O, the activity for nitrous oxide removal was strongly inhibited by addition of NO. This is most probably due to a strongly adsorbed intermediate formed from nitrogen dioxide and the hydrocarbon. The catalytic activity was found to be slightly decreased upon addition of up to 7% water vapor. High nitrogen oxide conversions of more than 80% have been achieved during the simultaneous removal of N_2O and NO at 350°C under realistic off-gas conditions. In that case, a further treatment of the exhaust gas is necessary to remove unreacted hydrocarbon as well as carbon monoxide being formed in side reactions.

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